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FINAL REPORT

SYNTHESIS OF ORGANOFLUORINE COMPOUNDS  
BY DIRECT FLUORINATION

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this research is to utilize a new fluorination technique for making fluorocarbon oligomers and polymers. The work will provide methods for synthesizing monomers and oligomers useful in making fluorocarbon ether elastomers. The research is aimed at the utilization of a direct fluorination technique for the conversion of organic compounds, particularly oxygen-containing organic compounds to polymerizable difunctional perfluorinated monomers and oligomers.		

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# PUBLICATIONS

- 1- "The Successful Direct Fluorination of Oxygen-Containing Hydrocarbons", J. Org. Chem., 40, 3271 (1975) with J. L. Adcock and R. A. Beh.
- 2- "The Synthesis of Structurally Unusual Fluorocarbons by Direct Fluorination", J. Amer. Chem. Soc., 97, 513 (1975) with N. J. Maraschin, B. D. Catsikis, L. H. Davis and G. Jarvinen.
- 3- "Nitrogen Compounds as High Yield Precursors to Branched Fluorocarbons by Direct Fluorination", J. Fluorine Chem., Dec. (1975) with J. L. Adcock, B. D. Catsikis and J. W. Thompson.
- 4- "The Synthesis of Novel Fluorine Containing Small Carboranes and Bis(difluoroboryl)Methane", Inorganic Chemistry, 14, 1855 (1975) with N. J. Maraschin.
- 5- "The Synthesis of Perfluoro 1, 4-Dioxane, Perfluoro(Ethyl Acetate) and Perfluoropivaloyl Fluoride by Direct Fluorination", J. Amer. Chem. Soc., 96, 7588 (1974) with J. L. Adcock.
- 6- "The Synthesis of Perfluoroglyme and Perfluorodiglyme by Direct Fluorination", J. Org. Chem., 38, 3617 (1973) with J. L. Adcock.
- 7- "The Direct Fluorination of 2,2,4,4 Tetramethylpentane; Sterically Protected Residual Protons?", J. Org. Chem. (in press) with L. A. Shimp.
- 8- "Simultaneous Fluorination and Functionalization of Hydrocarbon Polymers", J. Amer. Chem. Soc. (in press) with J. L. Adcock and Shoji Inoue.

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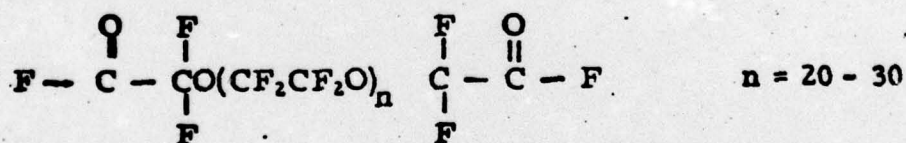
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- 4- L. H. Davis, Graduate Student, Department of Chemistry, University of California at Los Angeles.
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- 7- Dr. N. J. Maraschin, Union Carbide Corporation, Boundbrook, New Jersey.
- 8- Dr. L. A. Shimp, Research Assistant of Department of Chemistry, University of Texas at Austin.
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## THE SYNTHESIS OF NEW ORGANOFLUORINE COMPOUNDS BY DIRECT FLUORINATION

The major thrust during the first year of support by the Air Force Office of Scientific Research has been directed toward the projects originally mentioned in the Research Proposal. Most of these investigations have been very successful, and attached as an appendix to this report are several manuscripts which have been published or are now in press. These publications are definitive pieces of chemistry that establish conclusively that one can, with a very high degree of success, prepare perfluorinated oxygen-containing functional and difunctional compounds. Also, very well established is the fact that one can prepare fluorocarbons from hydrocarbons even in structurally challenging situations. We have obtained in much higher yield and often uniquely, new perfluorocarbon materials. It has therefore been established that the direct fluorination technique will provide analogs to basic organic compounds which are certain to be of much practical importance over the years in organic chemistry.

During the past year some of the most intense effort on this project has been directed to the preparation of perfluoropolyether oligamers by direct fluorination of hydrocarbon polyethers. The fluorination of high molecular weight polyethers under control conditions has resulted in the preparation of a series of oligamers which appear to have the structure:



These oligamers are believed to be difunctional and of prime interest to the Air Force Materials Program. It is thought that the length of polymer chain can be modified in either direction by altering the fluorination conditions. The degree of difunctionalization is being investigated by carbon-13 and fluorine-19 NMR techniques and methods are being developed for separation of non-functional and monofunctional perfluoroethers from the difunctional oligamers.



A major effort is also being directed toward the preparation of lower molecular weight volatile oligamers of the same structure. The high molecular weight material which was first obtained has excellent thermal properties, but unfortunately is insoluble in most organic and fluorocarbon solvents. The limited solubility makes it difficult to characterize and manipulate as a copolymer. Under more vigorous reaction conditions, volatile products are obtained which appear to be a source even of functional perfluoropolyethers of a single molecular weight and chain length. Such products appear to be attainable via separation of volatile products by preparative gas chromatography. Another ongoing effort involves base hydrolysis at high temperatures and cleavage of the higher molecular weight material to produce lower molecular weight functional perfluoropolyethers.

Recently, several additional areas of experimentation have been undertaken on this project. A concerted effort is being made to study the selective fluorination of organic compounds at very low temperatures. Thus, it may be possible to replace selected protons in organic compounds with fluorine with the hope of obtaining high yields of certain partially fluorinated organic compounds. The initial results in the area are promising, if not definitive.

An area of primary effort has been in the functionalization of polymer surfaces by fluorination of hydrocarbon polymers with an oxygen-fluorine mixture. If methyl or ethyl groups are bound to a polymer surface such as is the case in polypropylene or conventional (lower density) polyethylene, we have been able to functionalize these alkane groups as we perfluorinate the backbone of the polymer. The functionalization of polymer surfaces can be conducted efficiently on polymeric materials of any shape including fine powders, objects and surfaces of films. The fluorination penetrates 0.1 to 0.2 millimeter. In the case of polypropylene, from 10% to 65% of the methyl groups in a 100-mesh particle can be converted to acid fluorides during this fluorination process. This would indicate that nearly the entire methyl population of the surface is converted to the functional acid fluoride. The acid fluoride can be hydrolyzed easily to produce carboxylic acid groups



bound directly to the carbon chain over the total surface of a polymer. This difunctionalization research has applications in at least three areas: inert functionalized membranes for batteries and electrochemical cells, use as templates for synthesis in organic chemistry and biochemistry, and support of catalytically reactive materials. Thus, one can convert a homogeneous catalyst into a more useful heterogeneous catalyst, and overcome catalyst recovery problems. We have successfully bound the manganese pentacarbonyl to the surface of these polymers. The most recent efforts in this area involve preservation of polymer functional groups during fluorination and methods for preparing functionalized fluorocarbon surfaces via pendant perfluoropolyesters as intermediates.

Other areas presently under study include the preservation of silicon-carbon bonds during direct fluorination, the synthesis of perfluorocrown ethers, and the syntheses of a number of other structurally unusual fluorocarbons such as perfluorospirpentane.

New methods which have been recently developed for direct fluorination have enabled practical syntheses in high yields of oxygen-containing perfluorocarbons from their hydrocarbon analogs. These syntheses have been successful on several important classes of oxygen-containing hydrocarbons and most functional groups survive these gentle fluorinations. The syntheses of perfluoro-1,2-dimethoxyethane, perfluorobis(2-methoxyethyl)ether, perfluoro-1,2-diethoxyethane, perfluoro-1,4-dioxane, perfluoroethyl acetate, perfluorodimethylmalonyl difluoride, and perfluoropivaloyl fluoride from their hydrocarbon analogs are discussed. The monohydro species -hydrotetrafluoroethyl trifluoroacetate, monohydroctafluoropivaloyl fluoride, and 1-hydroxonafluoro-2,5-dioxahexane have also been prepared and characterized.

The reaction of elemental fluorine with structurally unusual hydrocarbon starting materials has been carefully controlled so that structurally analogous perfluorocarbons have been successfully obtained. The syntheses by direct fluorination of perfluoroneopentane, perfluorohexamethylethane, perfluorobornane, 1-hydrooundecafluoronorbornane, perfluorocyclooctane, and monohydropentadecafluorocyclooctane are reported.

The low temperature direct fluorination of highly branched nitrile and amine containing hydrocarbons were conducted under conditions conducive to good yields of perfluorinated hydrocarbons. Perfluoroneopentane was produced from pivalonitrile and perfluoroisobutane from t-butyl amine. The results suggest the lability of  $\text{NF}_2$  groups under the conditions of the experiment. In contrast, when normal nitriles, such as glutaronitrile and nitrogen containing ring compounds, such as morpholine are fluorinated, the corresponding nitrogen containing fluorocarbon is produced in higher yields than previously reported by other fluorination methods.

The first fluorine-containing smaller carboranes and bis(difluoroboryl)-methane have been prepared. The controlled reaction of  $\text{C}_2\text{B}_5\text{H}_7$  with elemental fluorine yields the new compounds  $\text{BF}_2\text{CH}_2\text{BF}_2$  (I), 3- $\text{FC}_2\text{B}_5\text{H}_6$  (II), 1- $\text{FC}_2\text{B}_5\text{H}_6$  (III), 5- $\text{FC}_2\text{B}_5\text{H}_6$  (IV), 1,5- $\text{F}_2\text{C}_2\text{B}_5\text{H}_5$  (V), 1,3- $\text{F}_2\text{C}_2\text{B}_5\text{H}_5$  (VI), and 5,6- $\text{F}_2\text{C}_2\text{B}_5\text{H}_5$  (VII). These new carboranes were characterized by B NMR spectroscopy, mass spectroscopy, and infrared spectroscopy.

The controlled reaction 2,2,4,4 - tetramethylpentane with fluorine at  $-78^\circ$  yielded three major products: 3,3-dihydrooctadecafluoro-2,2,4,4-tetramethylpentane, 3-hydroxoodecafluoro-2,2,4,4-tetramethylpentane and perfluoro-2,2,4,4-tetramethylpentane. These products were present in ratios of 0.14 to 0.66 to 0.20 respectively



with an overall yield of 70 - 95%. Evidence which suggests the methylene protons on the first two species are sterically protected by the bulky trifluoromethyl groups was obtained by noting that these compounds were not converted or fluorinated further to the perfluoro 2,2,4,4-tetramethylpentane by further reaction with fluorine.